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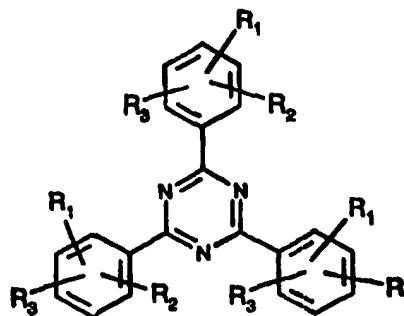
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<p>(21) International Application Number: PCT/EP97/06226 (22) International Filing Date: 10 November 1997 (10.11.97) (30) Priority Data: 2865/96 20 November 1996 (20.11.96) CH (71) Applicant (for all designated States except US): CIBA SPECIALTY CHEMICALS HOLDING INC. [CH/CH]; Klybeckstrasse 141, CH-4057 Basel (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): EHLIS, Thomas [DE/DE]; Ferdinand-Weiss-Strasse 30, D-79106 Freiburg (DE). HÜGLIN, Dietmar [DE/DE]; Sandstrasse 6, D-79104 Freiburg (DE). LUTHER, Helmut [DE/DE]; Tullingerweg 3a, D-79639 Grenzach-Wyhlen (DE). (74) Common Representative: CIBA SPECIALTY CHEMICALS HOLDING INC.; Patentabteilung, Klybeckstrasse 141, CH-4057 Basel (CH).</p>		<p>(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>

(54) Title: SYMMETRICAL TRIAZINE DERIVATIVES

(57) Abstract

A description is given of symmetrical triazine derivatives of formula (1), wherein R₁ and R₂ are each independently of the other hydrogen; C₁-C₁₂alkyl, C₁-C₁₂alkoxy; and R₃ is C₁-C₁₂alkyl; or C₁-C₁₂alkoxy. The easily accessible triazine derivatives are suitable for protecting ultraviolet-sensitive materials, in particular skin and hair of humans and animals, from the harmful effects of UV radiation.



(1)

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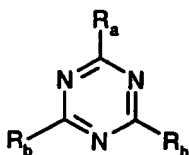
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Symmetrical triazine derivatives

The present invention relates to symmetrical triazine derivatives, to the preparation of these compounds as well as to their use for protecting organic materials from the harmful effects of UV radiation..

O-alkylated o-hydroxyphenyltriazines (HPT) containing at least one o-hydroxyl group or at least two alkoxyphenyl substituents are known, e.g. from EP-A-0,743,309, as cosmetic UV absorbers having good spectral properties and good technical application properties. However, the preparation of such triazine derivatives, which are derived from the

unsymmetrical basic structure

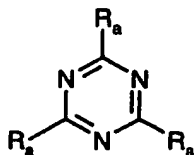


, requires multistep synthesis processes.

In the above formula, R_a and R_b are a reactive radical, in particular a phenyl radical which is mono- or polysubstituted by hydroxyl groups.

Symmetrical triazine compounds which may be prepared from the symmetrical basic

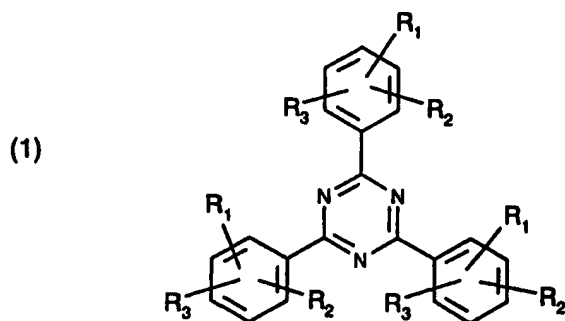
structure



are easier to access in simple one-bach processes.

Such "triazine basic structures" may be prepared, for example, by trimerising corresponding benzonitrile compounds or, starting from cyanuric chloride, by Grignard reaction or Friedel-Crafts alkylation. Subsequent etherification of the free OH groups makes it possible to prepare the desired triazine derivatives may be prepared in a two-step reaction.

Accordingly, this invention relates to symmetrical triazine derivatives of formula



wherein

R_1 and R_2 are each independently of the other hydrogen; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy; and R_3 is C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy.

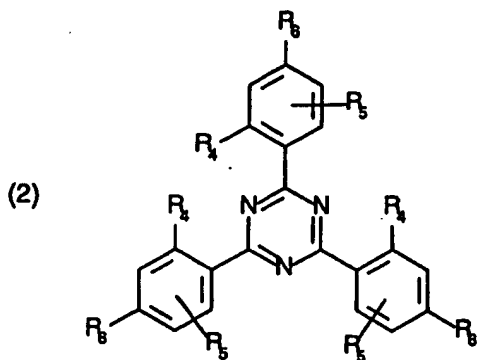
C_1 - C_{12} Alkyl or C_1 - C_{12} alkoxy are straight-chain or branched alkyl radicals, typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, amyl, isoamyl or tert-amyl, heptyl, octyl, isooctyl, nonyl, decyl, undecyl or dodecyl, or methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy or dodecyloxy.

Particularly preferred compounds are those of formula (1), wherein

R_3 is C_1 - C_{12} alkoxy, in particular C_5 - C_{12} alkoxy; and

R_1 and R_2 have the meaning given in formula (1).

Very particularly preferred compounds are those conforming to formula



wherein

R_4 and R_5 are each independently of the other hydrogen; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy; and

R_6 is C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy.

Important compounds are, in particular, those of formula (2), wherein

R₄ is hydrogen; and

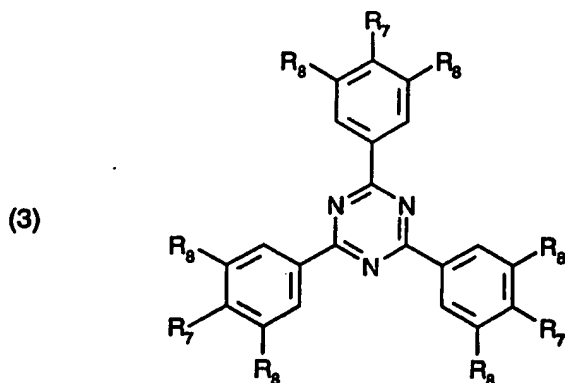
R₅ and R₆ are C₅-C₁₂alkoxy;

or those compounds of formula (2), wherein

R₄ and R₅ are C₅-C₁₂alkyl; and

R₆ is hydrogen.

Very particularly preferred compounds are those of formula



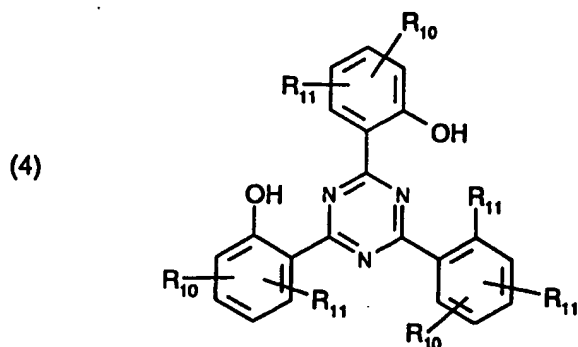
wherein

R₇ is C₅-C₁₂alkoxy; and

R₈ is hydrogen; or C₁-C₅alkyl.

The triazine derivatives of this invention can be used as single compounds or as mixtures of different single compounds with each other.

The novel symmetrical triazine derivatives of formula (1) can, in particular, also be used as mixtures with triazine compounds of formula



In formula (4),

R_{10} is hydrogen; C_6-C_{12} alkyl; or C_2-C_8 alkenyl; and

R_{11} is C_1-C_{12} alkoxy.

C_2-C_8 Alkenyl is, for example, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl or 3-methyl-but-2-enyl.

The mixtures of triazine compounds of formula (1) and formula (4) are another subject matter of this invention.

The novel triazine derivatives of formula (1) may be prepared in different manner. In a Grignard reaction, for example, 1 mol of cyanuric chloride is reacted with 3 mol of the corresponding phenylmagnesium bromide compound which, depending on the meaning of R_1 , R_2 and R_3 of formula (1), may contain an alkyl radical and/or one or several free hydroxyl groups. Processes for the preparation of this intermediate are known and are described, inter alia, in EP-A-0,557,559.

This intermediate is also obtainable by Friedel-Crafts alkylation of cyanuric chloride with the corresponding phenyl compounds which, depending on the meaning of R_1 , R_2 and R_3 in formula (1), may contain an alkyl radical and/or one or several free hydroxyl groups, in the presence of a Lewis acid, preferably aluminium chloride.

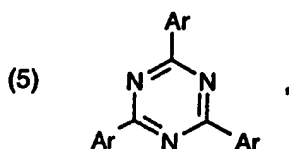
According to A. Ninagawa, M. Kawazoe, H. Matsuada, Makromol.Chem. 180, (1979), 2123, this intermediate is also obtainable by cyclotrimerisation of a benzonitrile compound con-

taining an alkyl radical and/or one or more than one hydroxyl group, depending on the meaning of R_1 , R_2 and R_3 in formula (1).

The end products corresponding to formula (1) are obtainable in a second reaction step by etherifying the hydroxyl group of the intermediates obtained in the first reaction step by alkylation in accordance with customary methods.

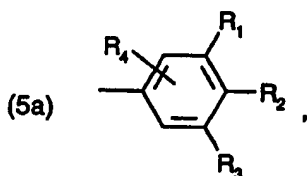
A further subject matter of this invention relates to the processes for the preparation of the novel triazine derivatives.

The inventive symmetrical triazine derivatives of formula (1) or mixtures of these compounds with triazine compounds of formula (4) as well as compounds of formula



wherein

Ar is a radical of formula



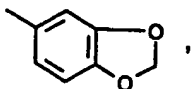
R_1 is hydrogen; hydroxy; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy;

R_2 is hydroxy; C_1 - C_{12} alkoxy; or benzyloxy;

R_3 is hydroxy; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy; and

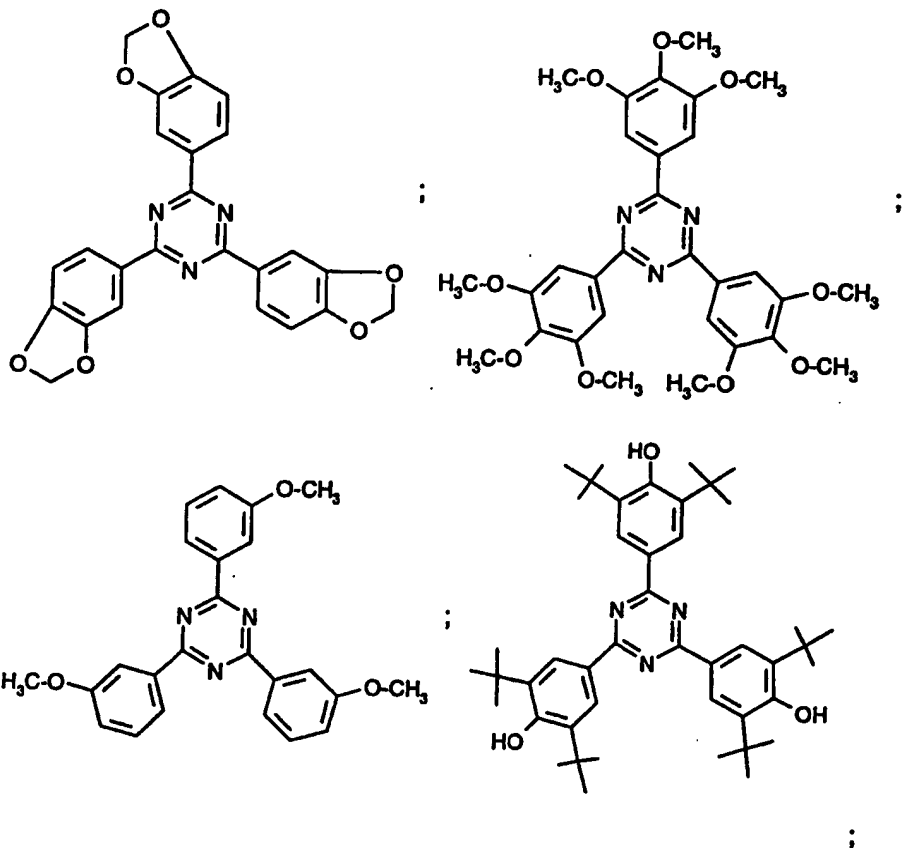
R_4 is hydrogen; or C_1 - C_{12} alkoxy; or

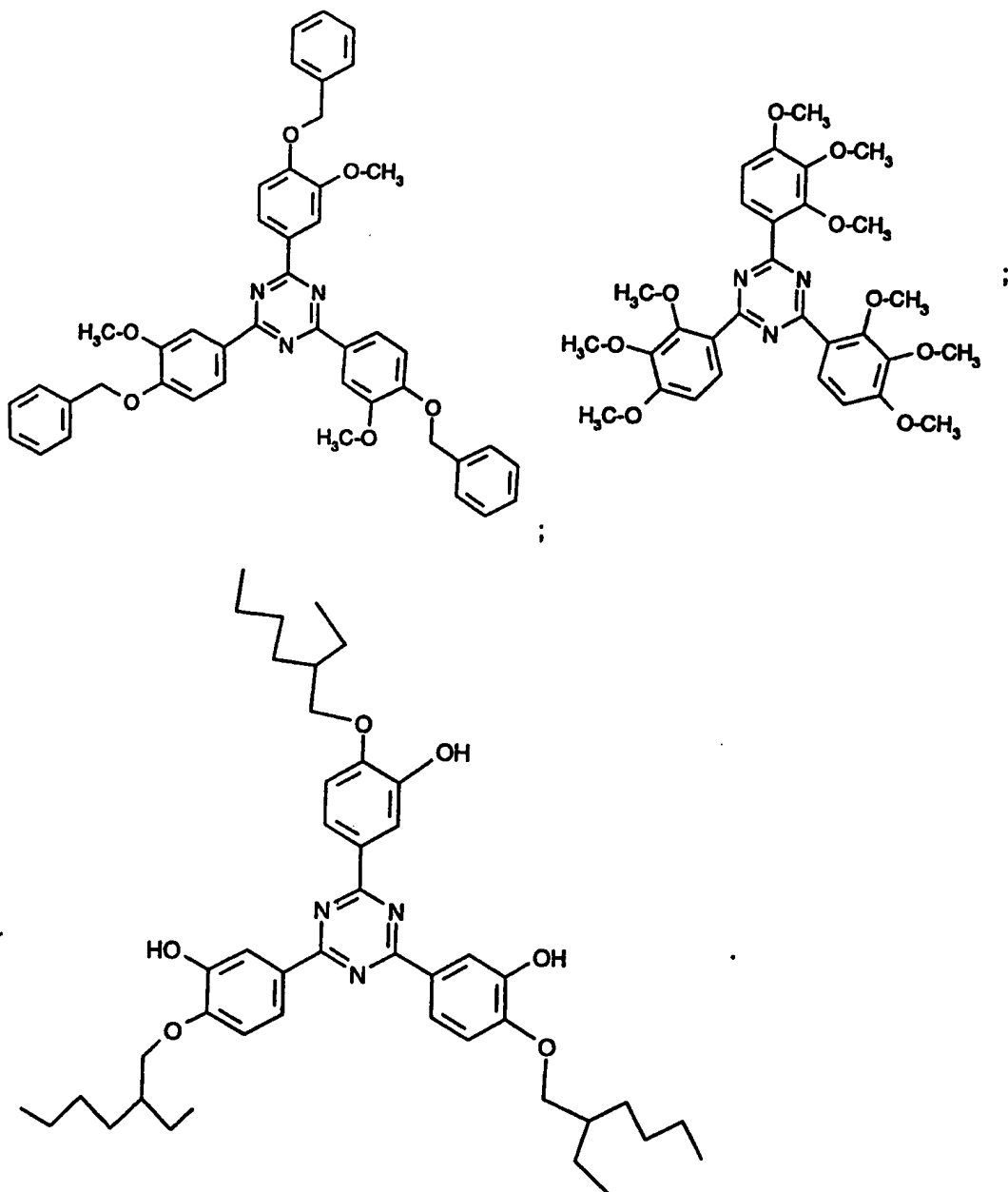
R_1 and R_2 , together with the phenyl radical, are a heterocyclic five-membered ring which is

condensed with benzene, preferably a radical of formula (5a) 

are particularly suitable as UV filters, i.e. for protecting ultraviolet-sensitive organic materials, in particular the skin and hair of humans and animals, against the harmful effects of UV radiation.

Illustrative examples of compounds of formula (5) are





Accordingly, these compounds are suitable as light stabilisers in cosmetic, pharmaceutical and veterinary preparations. They can be obtained in dissolved form or, if they are only sparingly soluble or insoluble, they can be incorporated in the preparations in micronised form having an average particle size in the range of 0.02 to 2, preferably of 0.05 to 1.5 and, most preferably, of 0.1 to 1.0 μm .

Accordingly, another object of this invention is the provision of a cosmetic preparation for skin or hair, which comprises at least one compound of formula (1) or (5) as well as carriers or auxiliaries which are cosmetically compatible with skin and hair, or to a cosmetic formulation for skin or hair, which comprises a mixture of

- a) at least one or more than one compound of formula (1) or (5), and
- b) a compound of formula (4).

together with carriers or auxiliaries which are cosmetically compatible with skin and hair.

In addition to the novel UV absorbers, the cosmetic formulations can also contain one or more than one further UV protective of the following substance classes:

1. p-aminobenzoic acid derivatives, typically 2-ethylhexyl 4-dimethylaminobenzoate;
2. salicylic acid derivatives, typically 2-ethylhexyl salicylate;
3. benzophenone derivatives, typically 2-hydroxy-4-methoxybenzophenone and its 5-sulfonic acid derivative;
4. dibenzoylmethane derivatives, typically 1-(4-tert-butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione;
5. diphenylacrylates, typically 2-ethylhexyl-2-cyano-3,3-diphenylacrylate and 3-(benzofuranyl)-2-cyanoacrylate;
6. 3-imidazol-4-yl-acrylic acid and 3-imidazol-4-yl-acrylate;
7. benzofuran derivatives, preferably 2-(p-aminophenyl)benzofuran derivatives, disclosed in EP-A-582,189, US-A-5,338,539, US-A-5,518,713 and in EP-A-613,893;
8. polymeric UV absorbers, such as the benzylidenemalonate derivatives described, inter alia, in EPA-709,080;
9. cinnamic acid derivatives, typically the 2-ethylhexyl 4-methoxycinnamate or isoamylate or cinnamic acid derivatives disclosed, inter alia, in US-A-5,601,811 and WO 97/00851;
10. camphor derivatives, typically 3-(4'-methyl)benzylidenebornan-2-one, 3-benzylidenebornan-2-one, N-[2(and 4)-2-oxyborn-3-ylidenemethyl]benzyl]acrylamide polymer, 3-(4'-trimethylammonium)benzylidenebornan-2-one methyl sulfate, 3,3'-(1,4-phenylenedimethine)-bis(7,7-dimethyl-2-oxo-bicyclo-[2.2.1]heptane-1-methansulfonic acid) and the salts thereof, 3-(4'-sulfo)benzylidenebornan-2-one and the salts thereof;
11. trianilino-s-triazine derivatives, typically 2,4,6-trianiline-(p-carbo-2'-ethyl-1'-oxi)-1,3,5-triazines as well as the UV absorbers disclosed in US-A-5,332,568, EP-A-517,104, EP-A-507,691, WO 93/17002 and EP-A-570,838;

- 12. 2-hydroxyphenylbenzotriazole derivatives;
- 13. 2-phenylbenzimidazole-5-sulfonic acid and the salts thereof;
- 14. menthyl-o-aminobenzoate;
- 15. TiO₂ (coated differently), ZnO and mica.

The UV absorbers described in "Sunscreens", Eds. N.J. Lowe, N.A. Shaath, Marcel Dekker, Inc., New York and Basel or in Cosmetics & Toiletries (107), 50 et seq. (1992), can also be used as additional UV protectives in the inventive formulations.

The cosmetic formulations can also be used together with known antioxidants, such as vitamin E, carotinoids or HALS compounds.

The novel cosmetic formulations usually comprise 0.1 to 25, preferably 0.5 to 10, % by weight, based on the total weight of the formulation, of a UV absorber of formula (1) or (5) or of a mixture of UV absorbers of formula (1) and formula (4) and a cosmetically compatible auxiliary.

The cosmetic formulations can be prepared by physically mixing the UV absorber(s) with the auxiliaries by conventional methods, such as by simply stirring the individual components together.

The cosmetic formulations of this invention can be formulated as water-in-oil or oil-in-water emulsion, as oil-in-alcohol lotion, as vesicular dispersion of a ionic or nonionic amphiphilic lipid, as gel, solid stick or as aerosol formulation.

As water-in-oil or oil-in-water emulsion, the cosmetically compatible auxiliary preferably comprises 5 to 50% of an oil phase, 5 to 20% of an emulsifier and 30 to 90% of water. The oil phase can contain any oil suitable for cosmetic formulations, for example one or several hydrocarbon oils, wax, natural oil, silicone oil, fatty acid ester or fatty alcohol. Preferred mono- or polyols are ethanol, isopropanol, propylene glycol, hexylene glycol, glycerol and sorbitol.

Cosmetic formulations for hair can be present

- in the form of a shampoo, lotion, gel or emulsion for rinsing, before or after shampooing, before or after dyeing or removing dye, before or after a perming or straightening process,
- in the form of a lotion, foam or gel for setting or treating hair,
- in the form of a lotion or gel for brushing or waving hair,
- in the form of a hair lacquer,
- in the form of a composition for perming or straightening hair, for dyeing or removing dye.

It is possible to use, for example, the following cosmetic formulations for hair:

- a₁) spontaneously emulsifying stock formulations, consisting of the UV absorber, PEG-6 C₁₀oxoalcohol and sorbitan esquioleate, which is charged with water and any quaternary ammonium compound, such as 4% minkamidopropyldimethyl-2-hydroxyethyl ammonium chloride or Quaternium 80;
- a₂) spontaneously emulsifying stock formulation, consisting of the UV absorber, tributyl citrate and PEG-20 sorbitan monooleate, which is charged with water and any quaternary ammonium compound, such as 4% minkamidopropyldimethyl-2-hydroxyethyl ammonium chloride or Quaternium 80;
- b) quat-doped solutions of the UV absorber in butyl triglycol and tributyl citrate;
- c) dispersions of micronised UV absorbers obtained by known methods (precipitation from solutions or mixtures of solutions, grinding), having an average diameter of 0.05 - 1.0 µm in APG (e.g. Plantaren), and a quat (e.g. minkamidopropyldimethyl-2-hydroxyethyl ammonium chloride) in an aqueous formulation;
- d) mixtures or solutions of the UV absorber with n-alkylpyrrolidone.

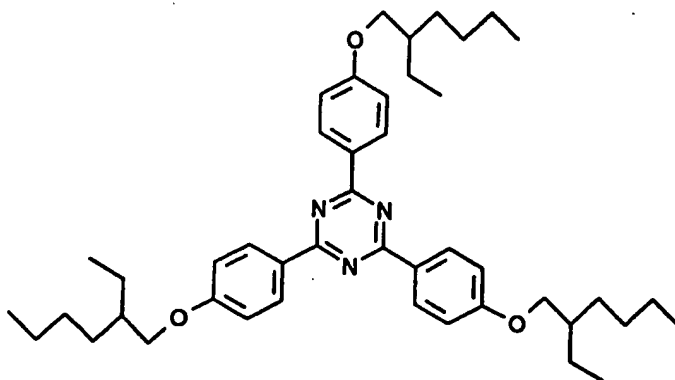
The cosmetic formulations for skin or hair may also contain other components, such as emollients, emulsion stabilisers, skin moisturisers, suntan promoters, thickeners, such as xanthan, moisture retention agents, such as glycerol, preservatives, fragrances and colourants.

The novel cosmetic formulations for skin or hair are distinguished by excellently protecting human skin and hair against the harmful effects of sunlight.

The following non-limitative Examples illustrate the invention in more detail. Percentages are by weight.

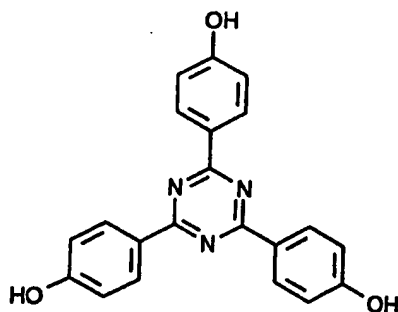
Example 1: Preparation of 2,4,6-tris(4-2-ethylhexyloxyphenyl)-(1,3,5)-triazine

(101)



The basic structure of formula

(101a)



is prepared by cyclotrimerising p-hydroxy-

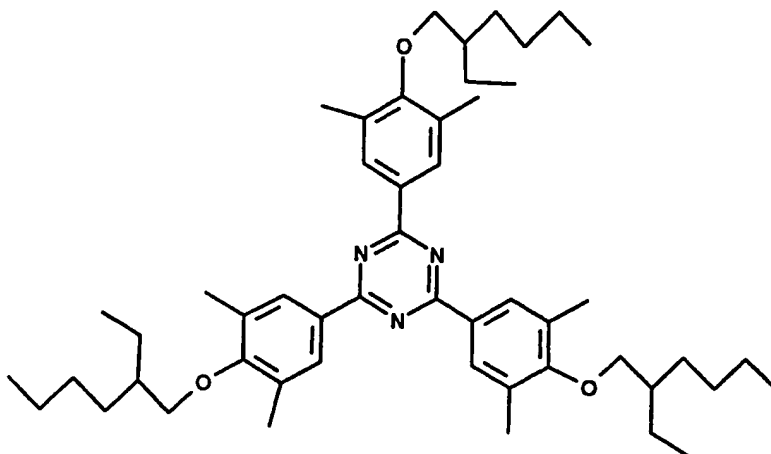
benzonitrile according to A. Ninagawa, M. Kawazoe, H. Matsuda, Makromol. Chem. 180 (1979), 2123.

5.36g of the compound of formula (101a) are dissolved in 50ml of dimethylformamide (DMF) and are charged with 6.53 g of finely powdered potassium carbonate at 100-105°C. This mixture is stirred for 30 minutes and then 8.23g of 3-(chloromethyl)heptane, dissolved in 10ml of DMF, are added dropwise over another 30 minutes at 100-105°C. The temperature is slowly elevated to 135°C over 6 hours. After cooling to 100°C, 50ml of toluene are added and the precipitated salts are removed by filtration. The filtrate is concentrated to dryness by evaporation and the residue is taken up with 50 ml of toluene and 100ml of water, acidified and extracted by shaking. The dried organic phase is concentrated by evaporation. The crude product (c. 7g) is purified by column chromatography (silica gel, cyclohexane/toluene 7:3).

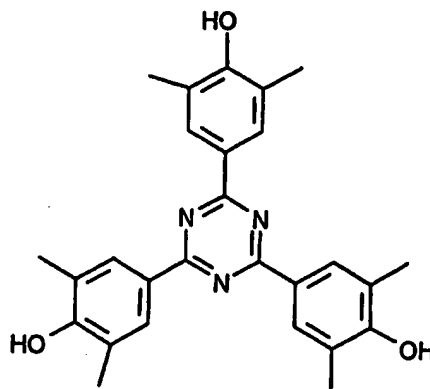
Yield: 4.8 g of colourless oil (46% of theory).

Example 2: Preparation of 2,4,6-tris[3,5-dimethyl-4-(2-ethylhexyloxyphenyl)]-(1,3,5)-triazine

(102)



The basic structure of formula (102a)



is obtained, for

example, by reacting 2,6-dimethylphenol with cyanuric chloride under Friedel-Crafts conditions (cf DE-A-2,219,012).

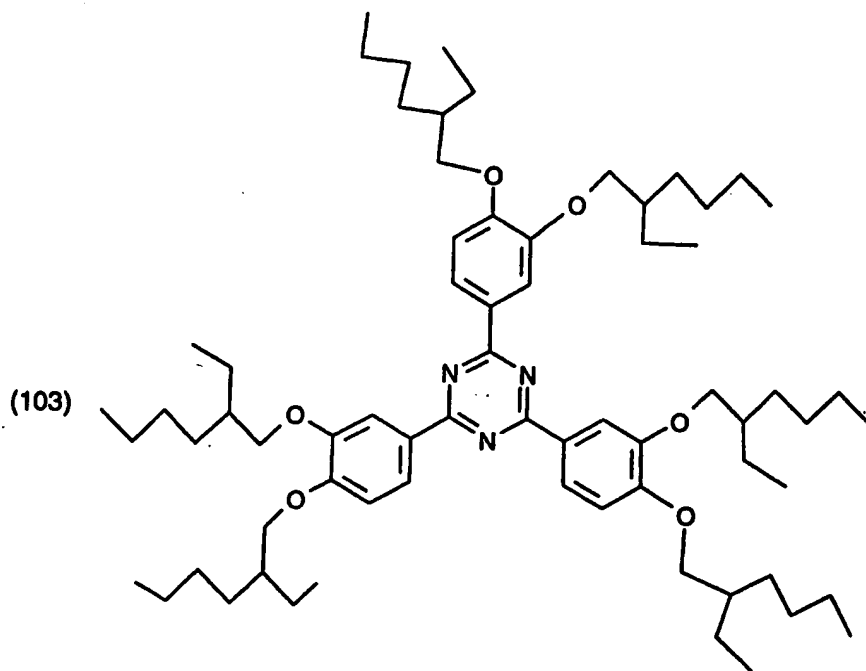
6.62 g of the compound of formula (102a) are dissolved in 70ml of dimethylformamide and are charged with 6.53 g of finely powdered potassium carbonate at 100-105°C. This mixture is stirred for 30 minutes and then 11.65 g of 3-(chloromethyl)heptane, dissolved in 10ml of DMF, are added dropwise over another 60 minutes at 100-105°C. The temperature is kept at 100-105°C for 3 hours. After cooling to 100°C, 50ml of toluene are added and the precipitated salts are removed by filtration. The filtrate is concentrated to dryness by evaporation and the residue is charged with 100 ml of toluene and 100ml of water, acidified and extracted by shaking. The organic phase is washed with water until neutral, separated,

dried and concentrated by evaporation. The crude product (c. 10g) is purified by column chromatography (silica gel, cyclohexane/toluene 65:35).

Yield: 4.7g of colourless crystals, m.p. 83-84°C, (40% of theory).

Example 3:

The compounds of formula



can be prepared in general analogy to the procedure of Example 1.

Use Examples:Example 4: Preparation of an O/W emulsion

Formulation (names according to CTFA or INCI):

(a ₁) cetareth 6 (and) stearyl alcohol	2.0%
(a ₂) cetareth 25	2.0%
(a ₃) cetaryl alcohol	5.0%
(a ₄) caprylic/capric triglyceride	5.0%
(a ₅) cetaryl octanate	10.0%
(a ₆) Vaseline	5.0%
(a ₇) compound of formula (101)	4.0%
(b ₁) propylene glycol	3.0%
(b ₂) carbopol 934	0.2%
(b ₃) H ₂ O	63.53%
(c) triethanol amine	0.27%

Components (a₁)-(a₇) (= phase A) and (b₁)-(b₃) (= phase B) are heated to 75-80°C. Phase B is then added to phase A and homogenised. Component (c) (= phase C) is then added and again homogenised.

The sunscreen factors are determined by the method of Diffey and Robson, J. Soc. Cosmet. Chem. 40, 127 - 133 (1989) using an SPF (sunproof factor) analyser (Optometrix, SPF 290).

This O/W emulsion has a sunscreen factor of 7.8.

Example 5: Preparation of a suntan cream:

Formulation (the individual components are named according to CTFA or INCI):

Phase A:

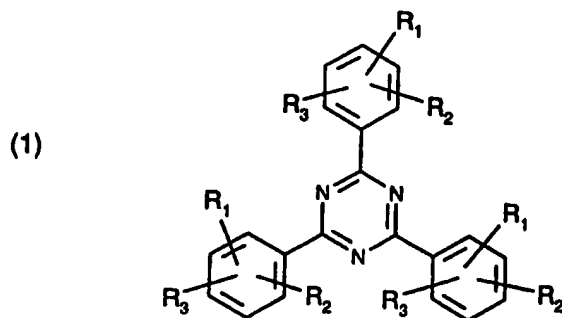
(a ₁) dimethicone	2.0%
(a ₂) isopropyl myristate	9.0%
(a ₃) stearyl alcohol	10.0%
(a ₄) stearic acid	4.0%
(a ₅) compound of formula (102)	4.0%
(a ₆) micronised 2,4-bis(phenyl)-6-(2-hydroxy-4-methoxyphenyl)-(1,3,5)-triazine (Ø 0.25 µm)	3.2 %
(b ₁) triethanol amine	1.2 %
(b ₂) carbomer 934 (1%)	5.0 %
(b ₃) H ₂ O	61.6 %

Components (a₁-a₆) (= phase A) are homogenised separately and very carefully and are then, like components (b₁)-(b₃) (= phase B), heated separately to 75-80°C. Phase B is then added to phase A with vigorous stirring. With stirring, the mixture is allowed to cool.

This suntan cream has a sunscreen factor of 11.

What is claimed is

1. A compound of formula



wherein

R₁ and R₂ are each independently of the other hydrogen; C₁-C₁₂alkyl, C₁-C₁₂alkoxy; and R₃ is C₁-C₁₂alkyl; or C₁-C₁₂alkoxy.

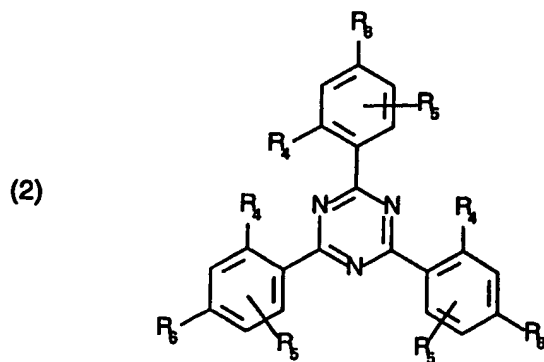
2. A compound according to claim 1, wherein, in formula (1),

R₃ is C₁-C₁₂alkoxy.

3. A compound according to either claim 1 or claim 2, wherein

R₃ is C₅-C₁₂alkoxy.

4. A compound according to claim 1 of formula



wherein

R₄ and R₅ are each independently of the other hydrogen; C₁-C₁₂alkyl; or C₁-C₁₂alkoxy; and R₆ is C₁-C₁₂alkyl; or C₁-C₁₂alkoxy.

5. A compound according to claim 4, wherein

R_4 is hydrogen; and

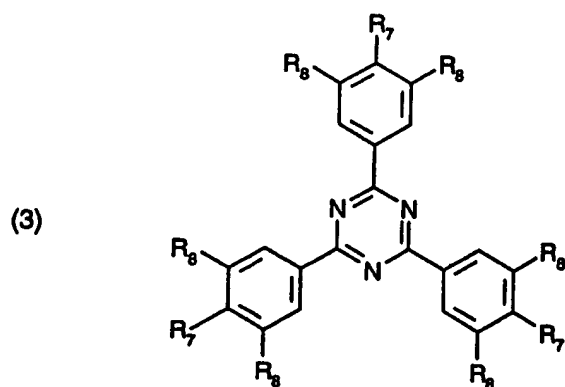
R_5 and R_6 are C_5 - C_{12} alkoxy.

6. A compound according to claim 4, wherein

R_4 and R_5 are C_5 - C_{12} alkoxy; and

R_6 is hydrogen.

7. A compound according to either claim 1 or claim 3 of formula

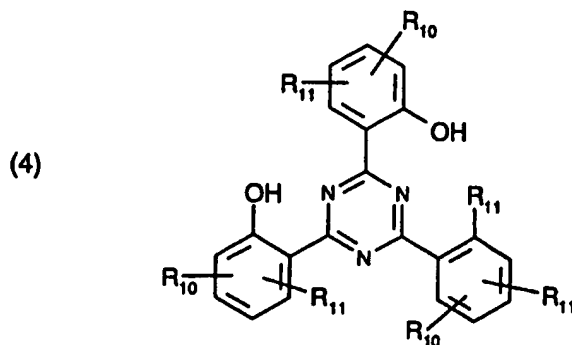


wherein

R_7 is C_5 - C_{12} alkoxy; and

R_8 is hydrogen; or C_1 - C_5 alkyl.

8. A mixture of the compounds of formula (1) and of formula



wherein

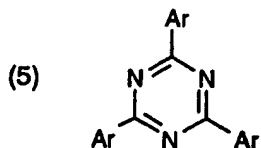
R_{10} is hydrogen; C_6 - C_{12} alkyl; or C_2 - C_6 alkenyl; and
 R_{11} is C_1 - C_{12} alkoxy.

9. A process for the preparation of the compounds of formula (1) according to claim 1, which comprises reacting in a first reaction step 1 mol of cyanuric chloride with 3 mol of the corresponding phenylmagnesium bromide compound which, depending on the meaning of R_1 , R_2 and R_3 in formula (1), can contain an alkyl radical and/or one or more than one free hydroxyl group, and etherifying in a second reaction step the free hydroxyl groups in an alkylation reaction.

10. A process for the preparation of the compounds of formula (1) according to claim 1, which comprises reacting in a first reaction step 1 mol of cyanuric chloride with 3 mol of the corresponding phenyl compound which, depending on the meaning of R_1 , R_2 and R_3 of the compound of formula (1), can contain an alkyl radical and/or one or more than one free hydroxyl group, by Friedel-Crafts alkylation in the presence of a Lewis acid and, in a second reaction step, etherifying the free hydroxyl groups in an alkylation reaction.

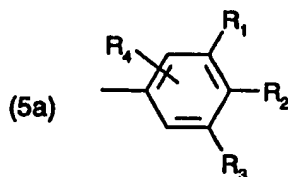
11. A process for the preparation of the compounds of formula (1) according to claim 1, which comprises cyclotrimerising in a first reaction step a benzonitrile compound which, depending of the meaning of R_1 , R_2 and R_3 in formula (1), can contain an alkyl radical and/or one or more than one hydroxyl group and, in a second reaction step, etherifying the free hydroxyl groups in an alkylation reaction.

12. Use of the compounds of formula (1) or



wherein

Ar is a radical of formula



R_1 is hydrogen; hydroxy; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy;

R_2 is hydroxy; C_1 - C_{12} alkoxy; or benzyloxy;

R_3 is hydroxy; C_1 - C_{12} alkyl; or C_1 - C_{12} alkoxy; and

R_4 is hydrogen; or C_1 - C_{12} alkoxy; or

R_1 and R_2 , together with the phenyl radical, are a heterocyclic five-membered ring which is condensed with benzene,

for protecting human and animal hair and skin from the harmful effects of UV radiation.

13. A cosmetic preparation for skin or hair, comprising at least one or more than one compound of formula (1) or (5) together with carriers or auxiliaries which are cosmetically compatible with hair and skin.

14. A cosmetic preparation for skin or hair, comprising a mixture of

a) at least one compound of formula (1) or (5), and

b) a compound of formula (4)

together with carriers or auxiliaries which are cosmetically compatible with hair and skin.

15. A cosmetic preparation for skin or hair according to either claim 13 or claim 14, which comprises at least 0.1 to 25 % by weight, based on the total weight of the formulation, of a UV absorber of formula (1) or (5) or of a mixture of UV absorbers of formula (1) and of formula (4) as well as at least one auxiliary which is compatible with skin and hair.

16. Use of the cosmetic preparation for hair according to any one of claims 13 to 15 for protecting hair from UV radiation, which is obtained in the form of a shampoo, lotion, gel or emulsion for rinsing, before or after shampooing, before or after dyeing or removing the dye, before or after a perming or straightening process, in the form of a lotion, foam or gel for setting or treating, in the form of a lotion, foam or gel for brushing or waving, in the form of a hair lacquer, in the form of a formulation for perming, dyeing or removing dye.

17. A process for treating human hair to protect it from the harmful effects of UV radiation, which comprises treating the hair with a shampoo, lotion, gel or emulsion for rinsing, before or after shampooing, before or after dyeing or removing the dye, before or after a perming or straightening process, with a lotion, foam or gel for setting, with a lotion, foam or gel for brushing or waving, with a hair lacquer, with a composition for perming or straightening hair, for dyeing or removing dye, which shampoo, lotion, gel, emulsion, foam, hair lacquer or composition for perming, straightening, dyeing or removing dye comprises at least one UV absorber of formula (1) or (5) or a mixture of a UV absorber of formula (1) and of formula (4).

INTERNATIONAL SEARCH REPORT

Internal I Application No

PCT/EP 97/06226

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C07D251/24 A61K7/42 A61K7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C07D A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>RUDENKO A P ET AL: "Oxidation of aromatic compounds. V. Oxidation of substituted benzonitriles and 2,4,6-triaryl-1,3,5-triazines in the HS03F-PbO2 system"</p> <p>ZH. ORG. KHIM. (ZORKAE,05147492);96; VOL.32 (10); PP.1499-1521, ST. PETERBURG. LESOTEKH. AKAD.;ST. PETERSBURG; RUSSIA (RU), XP002059474</p> <p>see compounds XIIf on page 1512, and Table 4, pages 1513-4, compounds XIIf,XIIf,XIIf,XIIf,XIIf.</p> <p>---</p> <p>-/--</p>	1,2,4

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

A document member of the same patent family

Date of the actual completion of the international search

19 March 1998

Date of mailing of the international search report

03. 04. 98

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Scruton-Evans, I

INTERNATIONAL SEARCH REPORT

Intern. Appl. Application No.

PCT/EP 97/06226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>ZHANG W M ET AL: "Cyclotrimerization of nitriles by the reactive alkali metal hydrides"</p> <p>CHIN. CHEM. LETT. (CCLEE7);95; VOL.6 (10); PP.839-42, CHINESE ACADEMY SCIENCES;DALIAN INSTITUTE CHEMICAL PHYSICS; DALIAN; 116023; PEOP. REP. CHINA (CN), XP002059475</p> <p>see compounds of Table 2, p-Me and m-Me and resulting triazine from Scheme 1, page 841</p>	1,4
X	<p>STUEBER G J ET AL: "Ultraviolet Stabilizers of the 2-(2'-Hydroxyphenyl)-1,3,5-triazine Class: Structural and Spectroscopic Characterization"</p> <p>J. PHYS. CHEM. (JPCHAX,00223654);95; VOL.99 (25); PP.10097-109, UNIVERSITAET STUTTGART;INSTITUTE FUER PHYSIKALISCHE CHEMIE; STUTTGART; D-70569; GERMANY (DE), XP002059476</p> <p>see Chart 2, page 10098, entries 2,3,11,12,14 and 15 and CN=103156-79-2 OLD, s-Triazine, 2,4,6-tris(p-OEtPh)</p>	1-4,7
X	<p>LLOBERA A ET AL: "Synthesis of s-triazines from aromatic aldehydes"</p> <p>SYNTHESIS (SYNTBF,00397881);85; (1); PP.95-8, UNIV. PALMA DE MALLORCA;FAC. CIENC.; PALMA DE MALLORCA; SPAIN (ES), XP002059477</p> <p>see compounds 4h and 4i on page 96 Table</p>	1,2,4
X	<p>BOYLE J T A ET AL: "Reactions of hydrazones and related compounds with strong bases. III. 1,2,4-Triazoles, 1,2,4-triazines, and 1,3,5-triazines from aromatic aldehyde azines"</p> <p>J. CHEM. SOC., PERKIN TRANS. 1 (JCPRB4);76; (2); PP.207-12, QUEEN'S UNIV. BELFAST;DEP. CHEM.; BELFAST; N. IRE., XP002059478</p> <p>see compound 9b</p>	1,2,4
X	<p>LANG U ET AL: "Preparation of aryl-substituted imidazoles"</p> <p>CHEM. BER. (CHBEAM);73; VOL.106 (6); PP.2079-81, UNIV. FREIBURG;INST. PHYS. CHEM.; FREIBURG/BR.; GER., XP002059479</p> <p>see compound 9, p2080</p>	1

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INTERNATIONAL SEARCH REPORT

Intern. Application No.

PCT/EP 97/06226

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CH 542 212 A (CIBA-GEIGY A.-G.) 15 November 1973 see column 32, ex 7,8, compound 154, column 36, and compound 159 starting material, 1,3,5-triazine, 2-[4-(1,1-dimethylethyl)phenyl]-4,6-bis(4-MePh), CN=16107-90-7 ---	1
X	ISHIKAWA T ET AL: "The Friedel-Crafts reaction of chloro-s-triazines with aromatic compounds and the synthesis of their derivatives. III. Reaction with xylenes" YUKI GOSEI KAGAKU KYOKAISHI (YGKKA); 67; VOL.25 (1); PP.55-9, TOKYO METROPOL. UNIV.; TOKYO; JAPAN, XP002059480 see Table on page 56, entries 1-3 ---	1
X	US 3 932 402 A (NORELL J R) 13 January 1976 see examples II, III, IV, VII ---	1,2,4
X	CH 539 101 A (CIBA-GEIGY A.-G.) 31 August 1973 ---	1
Y	see whole document, especially columns 11,12 ---	1-17
Y	EP 0 659 877 A (CIBA-GEIGY AG) 28 June 1995 see especially formulae 4 and 7, page 5, and pages 7/8 and claim 29. ---	1-17
P,Y	EP 0 743 309 A (CIBA-GEIGY AG) 20 November 1996 see whole document, especially p 16 ---	12-17
P,Y	WO 97 03643 A (CIBA SC HOLDING AG) 6 February 1997 ---	1-17
P,X	see especially page 3, and the definitions of R3,R4 and R5 on page 3. ---	12-15
X	BE 614 726 A (AMERICAN CYANAMID CO) 6 September 1962 SEE COMPOUND 2,4,6-TRIS(2,4-DiOMePh)triazine -----	1

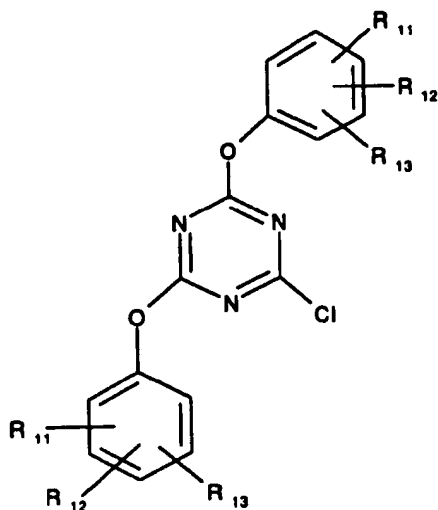
INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 97/06226

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CH 542212 A	15-11-73	NONE	
US 3932402 A	13-01-76	NONE	
CH 539101 A	31-08-73	NONE	
EP 659877 A	28-06-95	AU 684116 B AU 8160894 A BR 9405213 A GB 2285065 A JP 7216740 A NZ 270206 A ZA 9410243 A	04-12-97 29-06-95 01-08-95 28-06-95 15-08-95 28-08-95 23-06-95
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WO 9703643 A	06-02-97	AU 6519996 A GB 2303549 A	18-02-97 26-02-97
BE 614726 A		CH 407544 A DE 1469811 A FR 1318910 A GB 975966 A NL 275368 A US 3118887 A US 3268474 A	27-02-69 17-05-63 21-01-64 23-08-66



(VIII),

and step 1 run at -20°C to 200°C; at least one equivalent of the compound of formula IV is used in step 2, and 2.4 to twenty equivalents of the compound of formula VI are used per one equivalent of triazine in step 3.

15. A process according to claim 13 wherein

- step 1 is carried out in the presence of a base;
- step 2 is run neat in an excess of aromatic compound of formula IV;
- step 3 is carried out using only a protic acid as catalyst.

16. A process according to claim 13 wherein the phenolic compound of formula II and the compound of formula VI are identical and are of the formula

